THE EFFECT OF WEATHERING ON PILOTED IGNITION AND FLASH POINT OF A SLICK OF OIL

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N. Wu, T. Mosman, S.M. Olenick
and J.L. Torero
Department of Fire Protection Engineering
University of Maryland
College Park, MD, USA

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N. Wu, T. Mosman, S. M. Olenick and J. L. Torero
Department of Fire Protection Engineering
University of Maryland
College Park, MD,USA
E-mail: jltorero@eng.umd.edu , Telephone: 1-301-405-0043

Abstract

Ignition of a slick of oil on a water sub-layer has been experimentally studied. The objective of this work is to provide a tool that will serve to assess a fuels ease-to-ignite under conditions that are representative of oil spills. Two different techniques are used and the results compared, piloted ignition when the fuel is exposed to a radiant heat flux and flash point as measured by the ASTM D56 Tag Closed Cup Test. For the piloted ignition tests the fuel is exposed suddenly to external radiation to increase its temperature until ignition occurs. Temperature measurements and ignition delay time are used to characterize piloted ignition and an existing one-dimensional heat transfer model is used to correlate the experimental results. For the flash point test, the bulk temperature of the fuel is increased until thermal equilibrium is attained and then a pilot is introduced. The temperature at which the first flashes are observed is called the flash point. Two different crude oils were used for these experiments, ANS and Cook Inlet. Crude oils were tested in their natural state and at different levels of weathering. Piloted ignition and flash point are strong functions of the weathering level. Premature boiling of the water sub-layer inhibits ignition. The flash point temperature can be used as a characteristic pyrolysis temperature and the weathering level has a negligible effect on the thermal properties of the fuel. It was determined that a critical heat flux for ignition could be obtained and better serve as a parameter to characterize the fuel propensity to ignite in the presence of a strong pilot. The minimum heat flux that will permit ignition before boiling of the water sub layer occurs also needs to be considered.

1.0 Introduction

Burning of an oil spill is of interest as a result of offshore exploration, production, and transportation of petroleum (Koseki et al., 1991). In the case of an accidental spill at sea, in-situ burning can provide an effective means for the removal of an oil slick reducing negative environmental impact. The efficiency of the ignition and burning process is crucial for the successful elimination of the crude oil.

Information available on burning of a thin fuel layer on a water sub-layer is quite limited. Thin layer boil-over (Koseki et al., 1991, Garo et al., 1994, Arai et al, 1990) has been found generally to enhance the burning rate although Koseki et al. (1991) noted that boiling at the fuel-water interface can limit flame spread. The effect of minimum fuel layer thickness necessary for sustained combustion has been studied extensively (Garo et al., 1994, Arai et al, 1990). Several models have been developed to describe the heat losses from a pool fire to the supporting water layer (Brzustowski and Twardus, 1982) and to attempt a description of the in-depth absorption of radiation by the fuel layer (Twardus and Brzustowski, 1981). Flame spread across

the liquid fuel surface has also been emphasized and excellent review papers have been published by Glassman and Dryer (1980) and Ross (1994). Glassman and Drye (1980) summarize the extensive literature on ignition, however, it is clear that little attention has been drawn to characterize the ignition process of liquid fuels on a wate sub-layer.

Ignition behavior of petroleum fractions has not been studied beyond flash and fire points under quiescent conditions (Glassman and Dryer, 1980, SFPE Handbook, 1994, Hillstrom, 1975). The influence of weathering and the formation of oil/water emulsions on the flash and fire points have yet to be studied. Flash or fire point tests do not incorporate the effects that high heat insult has on the nature of the fuel, i.e. emulsions break down when subject to a high heat flux, thus are not sufficient to describe ignition in an oil spill scenario. Furthermore, heat transfer towards the water sub-layer is entirely dependent on the fuel properties and can preclude ignition, therefore needs to be incorporated when characterizing the ignition process. To the knowledge of the authors, the only study that addresses the effect of weathering and formation of emulsions on ignition under conditions pertinent to the oil-spill scenario is due to Putorti et al. (1994). This study was conducted in a cone calorimeter and quantified the necessary heat flux for ignition of various liquid fuels. In this work, emphasis was placed on the ignition delay time of weathered and emulsified samples.

Most accidental and deliberate burns of spilled oil at sea suffer from the effects of wind and waves. Volatiles tend to evaporate rapidly with time (weathering) and mixing tend to form oil/water emulsions making the oil difficult to ignite. Consequently, alteration of the physical or chemical properties of the oil can require additional energy for ignition. Several studies reported have attempted to characterize weathering and emulsions typical of oil-spill scenarios (Bobra, 1992).

In-situ burning of an oil spill requires the fuel to ignite and that ignition to be followed by spread and eventually leading to mass burning. Many studies have shown that ignition is not always followed by spread (Kashiwagi et al, 1997) therefore, is not sufficient to guarantee efficient removal of the oil slick. The need to understand the three stages necessary for the efficient removal of crude oil have resulted in the choice to use a modified version L.I.F.T., ASTM-E-1321 (ASTM Standards, 1994) apparatus to characterize the burning process.

Although the overall objective of this study is to characterize the entire burning process, the task is formidable. In the present work emphasis will be given to ignition. This choice does not provide optimal conditions for the study of each individual element but it is justified in the general context of this problem. This study will use two different crude oils (Cook Inlet and ANS) as representative of those commonly transported by oil-tankers. Crude oils will be studied in their natural state and subject to different levels of weathering. The formation of emulsions and its effect on ignition will be a subject of future study but goes beyond the objectives of the present work.

2.0 Background

2.1 Closed Cup Flash Point Test

The ASTM D56 Tag Closed Cup flash point tester was used to characterize the thermal properties under a controlled environment. The standard should be referenced for details of the apparatus (ASTM-Fire Test Standards, 1990). Flash point is defined as the lowest temperature corrected to a pressure of 760 mm Hg at which application of a test flame causes the vapors of a portion of the sample to ignite under specified conditions. The flash point measures the tendency of a fuel to form a combustible mixture with air under a controlled laboratory condition. It is only one of a number of properties that must be considered in assessing the overall thermal characteristics of a liquid fuel.

For the test for flash point, a liquid fuel is placed in the cup of the tester. With, the lid closed, the sample is heated up at a slow constant rate. A small flame of specified size is directed into the cup at regular intervals. The lowest temperature at which application of the flame ignites the vapors above the sample specifies the flash point. The flash point temperature gives an indication of the pyrolysis temperature of the fuel but not of the thermal properties that will lead to the attainment of this temperature. Therefore, the flash point temperature is of importance but not sufficient to describe the ignition process.

2.2 Piloted Ignition

Ignition of a combustible material can be accomplished in two ways. The first is by heating the material until ignition of the fumes occurs, this mechanism is commonly referred as spontaneous ignition. If the combustible material is only heated until the mixture between the fuel vapor and the ambient air reaches the lean flammability limit and ignition is achieved by means of a hot spot, this mechanism is called piloted ignition. For the specific application of in-situ burning piloted ignition will be the appropriate mechanism to consider.

Fuel properties vary significantly when subject to a strong heat insult, therefore, they need to be evaluated under "fire conditions." These properties are generally referred as "fire properties" (Quintiere, 1981). The concept of minimum heat flux for ignition has been commonly applied to solid fuels and ignition behavior can be predicted or measured using small, bench-scale experiments. In a similar fashion, ignition behavior of liquid fuels can be studied and evaluation of the "fire properties" allows ranking of fuels in various states; natural, weathered, and emulsified. The scale dependency will always be a matter of controversy, thus, large scale tests remain a necessity for validation. Yet, the number of tests needed to determine feasibility, protocols, and procedures for in-situ burning could be greatly reduced.

The mechanisms leading to gas phase ignition can be described as follows. The liquid bed is considered initially at ambient temperature, T_i. After suddenly imposing an external heat flux ($\dot{q}''_e$) the temperature of the bed rises until the surface reaches the pyrolysis temperature (T_p). The time required for the fuel surface to attain T_p will be referred the pyrolysis time, t_p. After attaining T_p, the vapor (pyrolysate) leaves the surface, is diffused and convected outwards, mixes with the ambient oxidizer, and creates a flammable mixture near the solid surface. This period will be

referred here as the mixing time , t_m. The flow and geometrical characteristics determine the mixing time. If the mixture temperature is increased the combustion reaction between the fuel vapor and the oxidizer gas may become strong enough to overcome the heat losses to the solid and ambient. Thus becoming self-sustained and at which point flaming ignition will occur. This period corresponds to the induction time, t_i, and is derived from a complex combination of fuel properties and flow characteristics.

Extending the analysis proposed by Fernandez-Pello (1995), the ignition time (t_{ig}) will be given then by

$$t_{ig} = t_p + t_m + t_i \qquad (1)$$

Under ideal conditions, introducing a pilot reduces the induction time making it negligible when compared to t_p and t_m. Furthermore, mixing has been commonly considered as a fast process compared to heating of the fuel, therefore, the fuel and oxidizer mixture becomes flammable almost immediately after pyrolysis starts. Pyrolysis temperatures and times are, thus, commonly referred as ignition temperature and ignition time (Quintiere, 1981) and equation (1) simplifies to

$$t_{ig} = t_p \qquad (2)$$

and T_{ig} can be defined as T_p. Although such a definition is not physically correct (Alvares and Martin, 1971) it can be very useful in some practical applications since provides a reference parameter that could serve to characterize ignition. In the present study the geometry will be chosen to make t_m and t_i minimal, thus $\dot{q}''_{0,p} \approx \dot{q}''_{0,ig}$ and, from equation (2), $t_p \approx t_{ig}$.

The flow over the fuel surface will control mixing of fuel and oxidizer as well as the transport of this mixture towards the pilot (t_m), therefore, can have a significant effect on t_{ig} and on the validity of equation (2). The relative effect of t_m on t_{ig} will decrease as the characteristic velocity of the system increases, characteristic time for mixing and transport decrease. Equation (2) could be extrapolated only if the experimental conditions at which the ignition delay time is obtained satisfy the assumption that $t_m \approx t_i \ll t_p$. Slight changes in the flow structure, especially for a horizontal configuration, can strongly affect t_m without changing t_p significantly. This effect will be least significant as the external heat flux approaches the critical heat flux for pyrolysis ($\dot{q}''_e \approx \dot{q}''_{0,p}$) and $t_p \to \infty$. This is important because it implies that the error incurred in the experimental determination of t_{ig}, (due to the unknown nature of the flow) will decrease as $\dot{q}''_e$ approaches $\dot{q}''_{0,p}$.

To obtain t_p the fuel and water bed are assumed as one thermally thick material with properties corresponding to an unknown combination of both liquids. The bed is assumed a semi-infinite slab, thus all convective and thermo-capillary motion in the bed is neglected. This assumption is not necessarily correct (Ross, 1994, Wu et al. 1997) but will be accepted as a possible source of error. Throughout the heating process the fuel layer is assumed inert with negligible pyrolysis before ignition. The

solution to the one-dimensional transient heating of a semi-infinite slab is given by Carslaw and Jaeger (1963) and an elaboration of all additional assumptions and the derivation pertaining to the present study are given by Quintiere (1981).

The boundary condition for this solution is imposed by heat balance at the surface which needs to incorporate convective heat losses, re-radiation, in-depth absorption and the fraction of the external heat flux not absorbed. Losses result in a minimum external heat flux necessary, $\dot{q}''_{0,p}$, to attain T_p. For $\dot{q}''_e < \dot{q}''_{0,p}$ the surface will attain thermal equilibrium at $T_{EQ} < T_p$.

A linearized heat transfer coefficient, h, is commonly used to describe heat transfer at the surface and all heat loss terms can be reduced to

$$\varepsilon\sigma(T^4 - T_\infty^4) + h_C(T - T_\infty) \approx h(T - T_\infty) \tag{3}$$

where h_C is the convective heat transfer coefficient, ε the emissivity of the fuel, σ the Stefan-Boltzmann constant ($\sigma = 5.67 \times 10^{-8}$ W/m^2.K^4) and T_∞ the ambient temperature. The value of "h" incorporates the convective heat losses, which depend on the present configuration, and the re-radiation from the surface of the fuel, which is only linked to the emissivity of the fuel, thus is a property of the fuel and needs to be evaluated under fire conditions. As expected, values for "h" have been shown to vary with orientation, fuel and environmental effects. Examples of typical values found in the literature are: 8.0 Wm^{2}K^{-1} for natural turbulent convection and a vertical sample (Quintiere, 1981), 13.5 Wm^{2}K^{-1} for a horizontal orientation (Janssens, 1991), and up to 15.0 Wm^{2}K^{-1} obtained by Mikkola and Wichman (1989) while conducting experiments on a vertical orientation with wood.

These assumptions lead to the following solution for the attainment of the pyrolysis temperature as a function of time (Quintiere, 1981, Wu et al. 1997)

$$h(T_p - T_i) = q''_e[1 - \exp(at_p)\text{erfc}(at_p)] \tag{4}$$

where t_p is the time necessary to attain T_p at the surface, $a = \alpha(h/k)^2$, "α" the thermal diffusivity and "k" the thermal conductivity. It needs to be noted that "k" and "α" are not the fuel or water properties but an equivalent set of properties that includes the contribution of both liquids. If $\dot{q}''_e = \dot{q}''_{0,p}$, T_p is expected to be reached when $t \rightarrow \infty$ and the critical heat flux that would lead to pyrolysis can be derived from equation (4) and is given by

$$\dot{q}''_{0,p} = h(T_p - T_i) \tag{5}$$

It has to be noted that equation (5) predicts a linear dependency between the pyrolysis temperature and the critical heat flux for ignition. The flash point temperature could be used as an approximate value for the pyrolysis temperature, therefore correlation between the critical heat flux for ignition and the flash point temperature will serve as validation for this approach.

For $\dot{q}_e'' >> \dot{q}_{0,p}''$ it can be assumed that $[1-\exp(at_p)\mathrm{erfc}(\sqrt{at_p})] \approx \frac{2}{\sqrt{\pi}}(at_p)^{1/2}$

which leads to the approximate expression valid for short times (t_p)

$$t_p = \frac{\pi}{4a}\left(\frac{\dot{q}_{0,p}''}{\dot{q}_e''}\right)^2 \tag{6}$$

Equation (6) is of great practical importance since shows that a plot of $t_p^{-1/2}$ as a function of the corresponding $\dot{q}_e''$ will be linear for $\dot{q}_e'' > \dot{q}_{0,p}''$ and from the slope of this line the value of "a" can be determined. The fire literature generally refers to "a" as a global thermal property.

3.0 Methodology

The Lateral Ignition and Flame Spread Test (LIFT- ASTM E-1321) has been extensively used to extract solid fuel "fire properties" under various heat insults originating from an external radiant energy source (Quintiere, 1981). The sample is positioned vertically, and a uniform radiant flux is suddenly applied. For this study the LIFT had to be rotated 90° to a horizontal position (figure 1). A fan, capable of inducing an air flow velocity of 0.1 m/s, was placed at the trailing edge of the sample. A homogeneous flow is guaranteed by means of a duct placed in front of the fan. The duct is filled with steel wool sandwiched between two honeycomb plates.
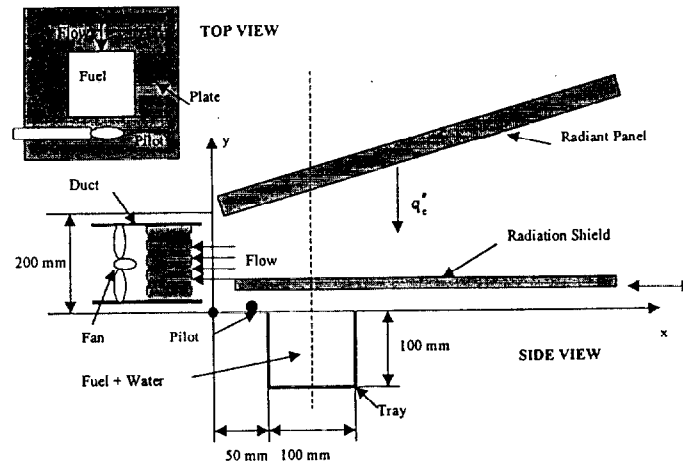

Figure 1   Schematic of the experimental apparatus.

A radiation shield (marinite board) is placed in front of the panel before the sample is introduced to its test position (figure 1). Once the sample has been placed, the radiation shield is removed and time recording starts. It was observed that differences between tests conducted under similar conditions increased as the distance

from the pilot to the fuel edge increased and as the size of the pilot decreased. In opposition, a thermocouple placed at the edge of the tray close to the fuel surface registered a heat contribution from the pilot as the pilot increased in size and was placed closer to the tray trailing edge. Thus, choice for size and location of the pilot resulted from a systematic study that minimized the effect of heat feed back from the pilot to the fuel surface and to guaranteed best repeatability of the results (Wu et al, 1997). Premature ignition by a pilot flame has been addressed by several authors who showed similar observations (Glassman and Dryer, 1980). This systematic study lead to small propane diffusion flame (20 mm in height) established on a 4 mm stainless-steel nozzle to be used as an ignition pilot. The nozzle was placed 10 mm above the fuel surface plane in the centerline and 10 mm downstream of the leading edge of the ignition tray (figure 1).

The fuel tray was placed under a 200 mm square plate with a 100 mm square hole in the middle where the fuel was located. Details on this plate and its use will be provided by Wu et al. (1997).

The radiant panel forms an angle of 15° with the sample, with the objective of producing a heat flux distribution as the one shown by Quintiere (1981). Despite the inclination the incident heat flux for the region up to 150 mm is relatively uniform providing a constant heat flux boundary condition for the fuel/air interface. Thermocouples measurements have been used to characterize the temperature evolution of the fuel and have shown neglectable differences at several locations along the fuel surface. Detailed hardware characteristics, typical heat flux distributions and experimental procedures involving the LIFT have been well documented (Quintiere, 1981, Wu et al. 1997) and will not be repeated here.

4.0 Experimental Results and Discussion

4.1 Ignition Delay Time

To calibrate the apparatus, SAE 30 W oil was first used for the ignition tests. This fuel was used to make possible comparison with previously reported results on ignition delay time (Putorti et al. 1994) and also because of the high flash point (approximately 250°C). The higher flash point results in a longer ignition delay time providing a longer period to observe the different processes affecting ignition. Radiation absorption is also lower with SAE 30 oil favoring boiling of the water bed. Although the viscosity of SAE 30 oil is generally higher than that of crude oils, it is very sensitive to temperature (approximately 1×10^{-2} $m^2 s^{-1}$ at 0°C and 1×10^{-5} $m^2 s^{-1}$ at 100°C) reaching comparable values after only a small temperature increase.

The results from these experiments are presented in Figure 2 together with data obtained for the same fuel by Putorti et al. (1994). Following equation (6) the ignition delay time is presented as $t^{-1/2}$. It can be observed that, although the ignition delay time significantly differs from the values found by Putorti et al. al. (1994) data converges to a unique critical heat flux for ignition. Since these experiments where conducted using different ignition procedures and under different environmental conditions, t_m is expected to be different, thus, affecting the ignition delay time. On the contrary, t_p should not be affected if convective losses are similar in magnitude or can be neglected. As the external heat flux approaches $\dot{q}''_{0,ig}$, t_m becomes neglectable

compared to t_p and all data converges to a unique point ($\dot{q}''_{0,ig} \approx 5\,kW/m^2$), as observed in Figure 2. This linear dependency corresponds well with data reported in the literature for solid fuels (Quintiere, 1981, Mikkola and Wichman, 1989) and serves to validate the above mentioned assumptions.
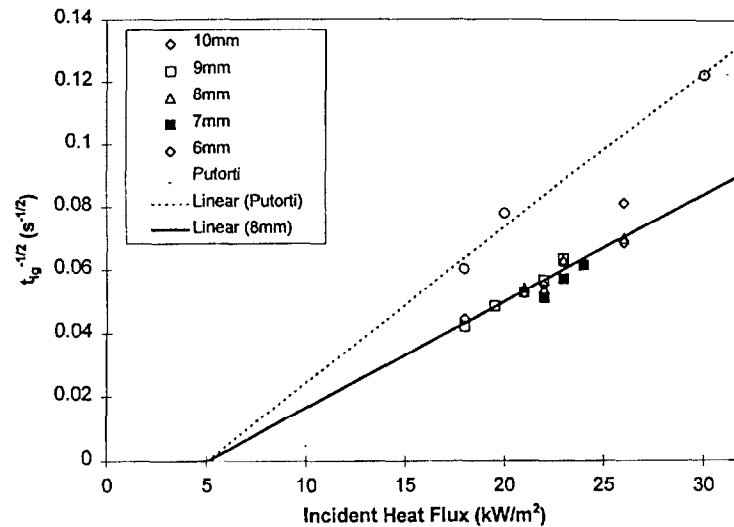

Figure 2 Ignition delay times for SAE 30W oil using the HIFT apparatus and Cone Calorimeter. The data corresponds to different heat fluxes and different fuel layer thickness.

For the particular case of an oil-slick on a water bed, the water underneath the fuel might attain boiling before ignition occurs. It was observed that once boiling started ignition of the fuel was precluded. Heating of the bed can be treated as a semi-infinite solid and temperature distributions can be predicted quite accurately (Brzustowski and Twardus, 1982). The analytical prediction of a characteristic time to boiling goes beyond the scope of this work. But, the determination of a minimum heat flux that will lead to boiling ($\dot{q}''_{0,B}$) before ignition can occur is of great practical importance therefore needs to be included as a complement to the critical heat flux for ignition.
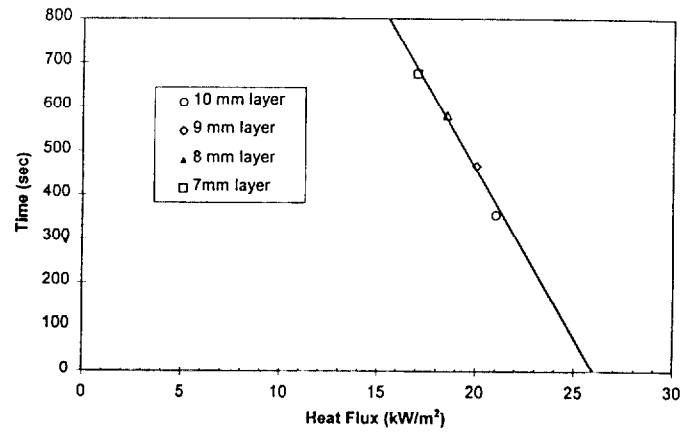
Figure 3. Critical heat flux to boil ($\dot{q}''_{0,B}$) for SAE 30W Oil using the HIFT Apparatus. The data corresponds to different fuel layer thickness an the time to the delay until boiling was attained.

As the external heat flux decreases the temperature gradient at the surface decreases and thermal penetration increases before the surface attains T_p. If the thermal wave can increase the water temperature at the fuel/water interface to the boiling point before the surface reaches T_p, boiling will prevent ignition from occurring. The minimum heat flux that will allow the surface temperature to reach T_p before boiling is given by $\dot{q}''_{0,B}$ and presented in figure 3. As the fuel layer decreases in thickness, the heat wave will reach the water faster allowing for a shorter available time for the surface to reach T_p and consequently requiring a higher temperature gradient at the surface (higher $\dot{q}''_{0,B}$).
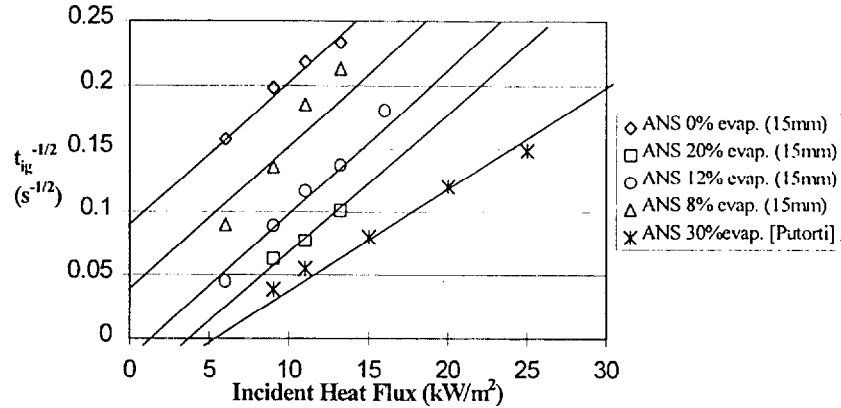

Figure 4. ANS crude oil ignition delay time for various levels of evaporation. The data corresponds to different heat fluxes and different fuel layer thickness.

4.2 Crude Oils and the Effect of Weathering

A series of tests were conducted with two crude oils. Figures 4 and 5 show ignition delay times for different external heat fluxes obtained for ANS crude oil, data reported by Putorti et al. (1994) and Cook Inlet crude oil. The data presented is an average of at least five experiments conducted under identical conditions. It was observed that ANS crude oil in its natural state ignited at ambient temperature, therefore no external heat flux was necessary. Flash points for this type of fuel have been reported as low as 19°C (SFPE Handbook, 1994) showing agreement with the above observation. When weathered, the ignition delay time decreases as the heat flux increases and a linear dependency between the external heat flux and $t_{ig}^{-1/2}$ is obtained. The intercept with the horizontal axis will provide the critical heat flux for ignition with negative values implying that the fuel will ignite at ambient temperature. Figure 4 shows that the critical heat flux for ignition will increase with weathering. When a line fit is made through the data corresponding to a specific mass loss it can be observed that these slopes remain invariant with the weathering level. The critical heat flux corresponding to the experimental data reported by Putorti et al (1994) fits well with the data collected in the present work. As previously mentioned the different experimental conditions account for the difference in slope.

Tests were conducted for different levels of evaporation and fuel layer thickness. Figure 5 corresponds to an example of the complete set of data for Cook Inlet crude oil. It is important to observe that for a fuel layer thicker than 8 mm the results are independent of this thickness. Systematic determination of the critical heat flux for ignition should be done using layers thicker than 8 mm. In contrast, it will be necessary to determine $\dot{q}_{0,B}''$ for all fuel layers.
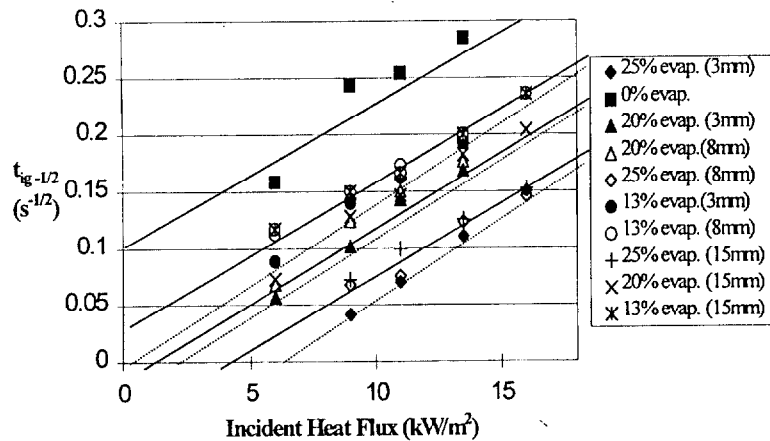

Figure 5. Cook Inlet ignition delay time for various levels of evaporation. The data corresponds to different heat fluxes and different fuel layer thickness.

As demonstrated by equation (6) the slope of the line fit to the data from presented in figures 4 and 5 provides the thermal property, "a", of the fuel. Figures 4 and 5 show that the slope remains invariant with the mass loss due to weathering. This is important since it proves that although the ignition event is controlled by the most volatile fractions of the crude oil, thus is affected by weathering, the heating process and the properties that characterize it are determined by the heavier fractions, thus invariant with weathering. In opposition figure 5 shows that the water bed has a significant influence on both the global thermal properties and the critical heat flux for ignition.

The critical heat flux for ignition ($\dot{q}''_{0,ig}$) as obtained from figures such as figure 4 and 5 is presented in figure 6. Results are presented for Cook Inlet and ANS crude oils for different fuel layer thickness. Figure 6 shows a discrepancy between the critical heat flux for ignition for 3 mm as opposed to almost identical values obtained for 8 and 15 mm layers. Thus, it can be verified that the fuel layer thickness affects the critical heat flux for ignition up to a thickness of 8 mm, with thicker layers resulting in almost identical results. The effect of fuel layer thickness was mostly manifested on the curves being truncated by boiling before attaining $\dot{q}''_{0,ig}$. The increasing value of $\dot{q}''_{0,ig}$ with mass loss shows that weathering makes ignition more difficult, the increasing slope of the curve points towards the possibility of an asymptotic value at which the crude oil will not ignite. Based on the values for $\dot{q}''_{0,ig}$ ANS crude oil was observed to be more prompt to ignition than Cook Inlet crude oil. Cook inlet ignited without an external heat flux for a mass loss rate smaller than 10 % and ANS crude oil for a mass loss smaller than 7%. The results presented are representative of all other cases studied.
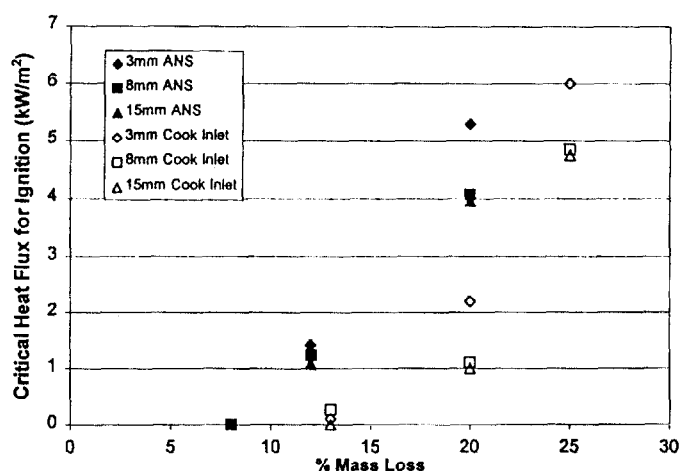

Figure 6. $\dot{q}''_{0,ig}$ for ANS and Cook Inlet crude oils as a function of the % mass loss due to weathering for various fuel layer thickness.

4.3 Flash Point Temperature

Results from flash point test for the crude oils as a function of the mass loss due to weathering are presented in figure 7. Each point in the figure represents the average of 10 tests conducted in accordance with ASTM D56 standard. As seen from the figure, flash points extracted using the ASTM D56 closed cup tester have a linear dependence on the level of evaporation for both crude oils. More importantly, the flash points for ANS crude oils are significantly higher than the Cook Inlet crude. Note that data is only presented for flash point temperatures above ambient (>20°C), since no ignition tests were conducted for temperatures lower than ambient. A mass loss greater than 20% has been demonstrated to need weeks of weathering under natural conditions (Ostazeski, 1996), therefore 20% will be used as an upper limit to the mass loss.
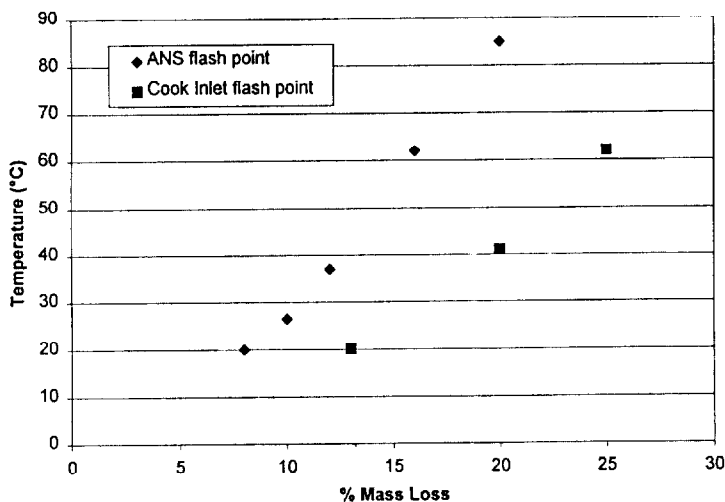

Figure 7. ASTM D56 Closed Cup Flash Point Temperature for ANS and Cook Inlet crude oils as a function of the % mass loss due to weathering.

Evaporation is the dominant weathering process that affects the crude oils in the marine environment. Depending on the conditions, the physical, chemical, and toxicological properties of a crude oil can be altered significantly by evaporation. Few references are available that provide sound results relating accelerated laboratory evaporation of crude oils to actual field conditions. Hydrocarbons constitute the mos important fraction in any crude oil. Although the proportions of each fraction varies significantly, (e.g. from 30-40% to 100% in gas condensates), they account for up to 70% in all petroleum on the average (Petrov, 1987). The light boiling fractions of standard crude oil can contain up to 150 different hydrocarbons. The complexity of petroleum hydrocarbon makes identification of individual elements difficult. However, in the early 1960's an elaborate analytical method was developed called ga chromatography-mass spectrometry. This allowed classification of fractions individual groups according to molecular structure: (1) Alkenes (C_5-C_{40}); (2) Napthenes or Cycloalkenes; and (3) Aromatic Hydrocarbons (Arenes).

The least complicated are the Alkenes, which are divided into three fractions. Fraction I is of primary interest since the C_5-C_{11} hydrocarbons are distilled from the crude oil at a temperature range of 30-200 °C. McAuliffe (1989) characterizes evaporation as a function of time to liberate the C_9 and lower hydrocarbons. The selection of this criteria is not arbitrary as the lighter fractions were not only the most likely to evaporate, but also the most biologically hazardous. This is the referencing standard to compare accelerated laboratory weathering to field conditions. Therefore, an analysis of only simple unsaturated hydrocarbons ($<C_{11}$) is made between individual petroleum fractions and weathered Cook Inlet and ANS crude oils. Complicated components such as saturated cyclic hydrocarbons (naphthenes) and aromatic hydrocarbons have been omitted because of the complex nature of these fractions. Weathering under very similar conditions as those presented here was conducted by Garo (1996) with a mixture of crude oils (63% Kittiway, 33% Arabian Light and 4% Oural) showing a variation of the flash point consistent with the above presented data. By means of gas chromatography Garo (1996) determined that hydrocarbons smaller than C_8 will be almost entirely evaporated before a mass loss of 10% is achieved. All these hydrocarbons have a flash point below 20°C, therefore the flash point of the weathered oil remained below this temperature. If 15% mass loss is attained hydrocarbons smaller than C_{10} are almost entirely evaporated. Flash point temperatures below 50°C characterize hydrocarbons in the range C_8 to C_{10}, thus the flash point of the weathered crude oil remains in this range. Further evaporation to approximately 20% leads to almost complete evaporation of hydrocarbons smaller than C_{16} resulting in an increase of the flash point to a value characteristic of these fractions (<80°C).

A comparison of the flash point temperature and critical heat flux for ignition as obtained by the HIFT ignition tests is presented in figure 8. The data points correspond to different levels of weathering. It can be noticed that the flash point temperature has a linear dependency with the critical heat flux for ignition ($\dot{q}''_{o,ig}$), as predicted by equation (5). The line fit, for ANS and Cook Inlet oils, converge to ambient temperature (20°C) for $\dot{q}''_{o,ig} = 0$. This observation is of great importance since it shows that the flash point temperature can be used as characteristic ignition temperature. Furthermore, by means of equation (5) the global heat transfer coefficient can be evaluated and corresponds to the slope of the line fit.

This information can be used in two ways. As shown by equation (3) the global heat transfer coefficient consists of radiative and convective components. The convective component is independent of the fuel, thus the slope of the data presented in figure 8 provides an indirect measure of the emissivity of the fuel. More important, if the global heat transfer coefficient (h) is known, and "a" is extracted from the ignition delay time, a "fire property," the product of the thermal conductivity, the density and the specific heat capacity ($k\rho C$) can be obtained.

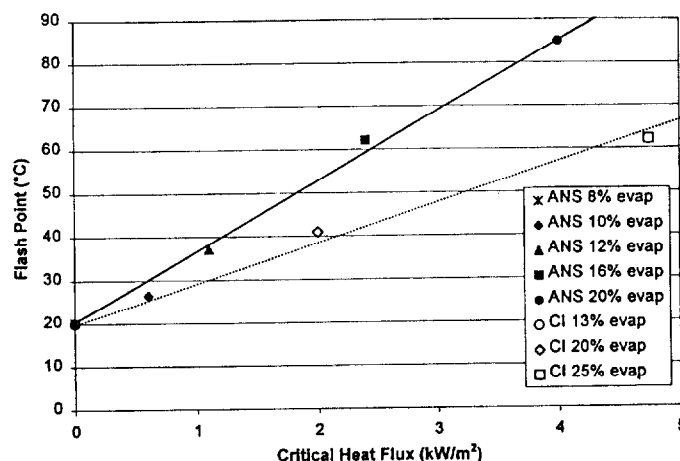$$(k\rho C) = \frac{h^2}{a} \tag{7}$$

Figure 8. Flash point temperature of ANS and Cook Inlet crude oils at various levels of weathering and as a function of the critical heat flux for ignition.

5.0 Conclusion

To study piloted ignition of a slick of oil on a water sub layer, a modified LIFT apparatus is used. As for solid fuels, ignition delay times and a critical heat flux for ignition of a liquid fuel supported by water can be extracted using this testing methodology. Open cup flash point temperature measurements are presented to complement the piloted ignition tests. The propensity of a crude oil to ignite can be characterized by three different parameters:

1. The critical heat flux for ignition ($\dot{q}''_{o,ig} \approx \dot{q}''_{0,P}$), it is independent of the environmental and experimental conditions and provides a measure of the minimum heat insult necessary to guarantee attainment of a pyrolysis temperature, thus production of enough gaseous fuel for ignition. The critical heat flux for ignition is obtain by extrapolation to $t_{ig} \rightarrow \infty$ of the ignition delay time data.

2. The critical heat flux for boiling ($\dot{q}''_{o,B}$), which provides a measure of the minimum heat flux necessary to attain ignition before boiling of the sub layer occurs.

3. The thermal "fire property" of the fuel (kρC) can be extracted from the ignition delay time in combination with the critical heat flux and provides a measure of the heating process. It is a function of the fuel and is independent of the experimental and environmental conditions.

4. Weathering affects the critical heat flux for ignition and the flash point temperature but has no effect on the "fire property" of the fuel (kρC).

The experimental methodology and its theoretical underpinnings were validated with SAE30W oil, ANS and Cook Inlet crude oils in its natural state and under different levels of weathering. The results show consistency and correlate well with other data present in the literature.

For a comprehensive evaluation of the ignition potential of a crude oil in an oil spill scenario the conclusions pertaining ignition should be accompanied by similar information on the characteristics of the flame spread and mass burning processes.

6.0 Acknowledgements

7.0 References

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